

AD-A243 433



2

OFFICE OF NAVAL RESEARCH  
Grant or Contract N00014-91WX-24155

DTIC  
S  
C  
D

R&T Code 4134053

Technical Report No. 6

Pressure Dependence of  $T_c$  in  $Tl_2Ba_2CaCu_2O_8$   
at Hydrostatic Pressures to 6 GPa

by

N. E. Moulton, S. A. Wolf, and E. F. Skelton  
U.S. Naval Research Laboratory  
Washington, DC 20375-5000

D. H. Liebenberg  
Office of Naval Research  
Arlington, VA 22217-5000

and

T. A. Vanderah  
Chemistry Division, Research Department  
Naval Weapons Center, China Lake, CA 93555

Submitted for publication in  
Phys. Rev. Lett.

October 1991

Reproduction in whole, or in part, is permitted for  
any purpose of the United States Government.

This document has been approved for public release  
and sale; its distribution is unlimited.

91-17386



91 1209 070

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE  
Oct 91

3. REPORT TYPE AND DATES COVERED  
Technical Report #6 10/90-9/91

4. TITLE AND SUBTITLE  
Pressure Dependence of  $T_c$  in  $Tl_2Ba_2CaCu_2O_8$  at Hydrostatic Pressures to 6 GPa

5. FUNDING NUMBERS  
N00014-91WX-24155

6. AUTHORS  
N. E. Moulton, S. A. Wolf, E. F. Skelton, D. H. Liebenberg, and T. A. Vanderah

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  
Naval Weapons Center  
China Lake, CA 93555-6001

8. PERFORMING ORGANIZATION  
REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  
Office of Naval Research (Chemistry Program)  
800 N. Quincy Street  
Arlington, Va 22217

10. SPONSORING/MONITORING  
AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Submitted to Phys. Rev. Lett.

12a. DISTRIBUTION /AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

We report the results of experiments carried out on single crystals of  $Tl_2Ba_2CaCu_2O_8$  under nearly hydrostatic pressure conditions to 6 GPa. The critical temperature,  $T_c$ , is observed to possess a non-linear pressure dependence. While the increase of  $T_c$  with increasing oxygen concentration in  $YBa_2Ca_3O_{7-\delta}$  is consistent with the observation of increasing  $T_c$  with increasing pressure, the  $Tl_2Ba_2CaCu_2O_8$  system demonstrates an increasing  $T_c$  with decreasing oxygen content, but has a positive  $dT_c/dP$  at low pressures. This behavior is clearly inconsistent with the picture applied to the YBCO system. In all the present measurements the curvature is downward and in fact for one sample it actually decreases. A theoretical explanation based upon the strong-coupling Eliashberg form of the BCS theory is put forth to explain this effect.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION  
OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION  
OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION  
OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

*Submitted to Phys. Rev. Lett.*

# **Pressure Dependence of $T_c$ in $Tl_2Ba_2CaCu_2O_8$ at Hydrostatic Pressures to 6 GPa**

**N. E. Moulton, S. A. Wolf, and E. F. Skelton**

U. S. Naval Research Laboratory  
Washington, DC 20375-5000

**D. H. Liebenberg**

Office of Naval Research  
Arlington, VA 22217-5000

**T. A. Vanderah**

Naval Weapons Center  
China Lake, California

and

**A. M. Hermann**

Department of Physics  
University of Colorado  
Boulder, Colorado

Accession For	
NTIS GRA&I	
DTIC TAB	
Unannounced	
Justification	
By	
Distribution	
Availability Codes	
Avail and/or	
Dist	Special
A-1	

## Abstract

We report the results of experiments carried out on single crystals of  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  under nearly hydrostatic pressure conditions to 6 GPa. The critical temperature,  $T_c$ , is observed to possess a non-linear pressure dependence. While the increase of  $T_c$  with increasing oxygen concentration in  $\text{YBa}_2\text{Ca}_3\text{O}_{7-\delta}$  is consistent with the observation of increasing  $T_c$  with increasing pressure, the  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  system demonstrates an increasing  $T_c$  with decreasing oxygen content, but has a positive  $dT_c/dP$  at low pressures. This behavior is clearly inconsistent with the picture applied to the YBCO system. In all the present measurements the curvature is downward and in fact for one sample it actually decreases. A theoretical explanation based upon the strong-coupling Eliashberg form of the BCS theory is put forth to explain this effect.

Studies of the pressure dependencies of the critical temperatures of hole-doped high  $T_c$  superconductors in the past have demonstrated, with very few exceptions, monotonically increasing  $T_c$ 's with increasing pressure.<sup>1,2</sup> This is thought to be due to the pressure-induced injection of holes onto the conduction planes resulting from a change in the apical Cu-O bond length,<sup>3,4,5</sup> a view consistent with the drop of critical temperature with decreasing oxygen concentration and hence decreasing hole concentration.<sup>6</sup> Recently work has been performed which indicates that for many of the thallium-based cuprates, increases in the oxygen content in as-made samples, actually decreases  $T_c$ ,<sup>7</sup> while decreases in oxygen content produce sharp increases in  $T_c$ , followed by decreases with further oxygen reduction.<sup>8</sup> However studies of the pressure dependence of  $T_c$  have indicated a positive slope at low pressures.<sup>9,10,11</sup> This effect is contrary to that observed for the YBCO systems.

In this *Letter*, we report the  $dT_c/dP$  results of experiments performed on several single crystals of  $Tl_2Ba_2CaCu_2O_8$  in a nearly hydrostatic environment to pressures of 6 GPa utilizing *in situ* pressure measurement techniques at low temperature. Two previous experiments with sintered samples have indicated that the pressure dependence of  $T_c$  in the Tl "2212" compound,  $Tl_2Ba_2CaCu_2O_8$ , may not be monotonic but rather increases with increasing pressure at lower pressures, reaches a maximum, and then decreases with further increasing pressure.<sup>12,13</sup> We also provide a theoretical explanation for the occurrence of the observed effects.

Samples were obtained from two preparation processes. Those in group A (samples later identified as having  $T_c(0)$  of 112.1, 107.2, and 106.7 K) were grown

in sealed gold capsules using the off-stoichiometric flux method. The oxides  $\text{Tl}_2\text{O}_3$ ,  $\text{BaO}_2$ ,  $\text{CaO}_2$ , and  $\text{CuO}$  were ground together for 45 min in a 2:2:3:4 molar metal ratio, respectively using an agate mortar and pestle. Approximately 3 g of the charge mixture was sealed in a gold capsule which was then heated under trapped flowing oxygen at 1 atm as follows: from ambient to 920 C in 1.5 h, soak 3 h, cool at 24 C/h to 750 C, furnace turned off and sample removed at room temperature. From the large number of black platelets embedded in a black polycrystalline matrix, an x-ray powder diffraction analysis was performed to determine the presence of the (2212) and (2223) phases in the approximate ratio of 60:40. Residual  $\text{BaCuO}_2$  and  $\text{CuO}$  were clearly present.

The preparation of the group B ( $T_c(0)$  of 114.1 K) began with appropriate amounts of  $\text{Tl}_2\text{O}_3$ ,  $\text{BaO}$ ,  $\text{CaO}$  and  $\text{CuO}$  (each 99.99% pure), these were ground to form a powder with a nominal composition of  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_x$ . The mixture was heated in air for 24 h at 920 C with an intermediate grinding carried out to facilitate a complete reaction. This powder was then pressed into a pellet under a load of 460 kg/cm<sup>2</sup>. Pellets of mass 25 g were placed in an  $\text{Al}_2\text{O}_3$  crucible, which was loosely covered by an  $\text{Al}_2\text{O}_3$  plate to protect the  $\text{Tl}_2\text{O}_3$  from direct evaporation. The crucible was then put into a quartz tube located in a horizontal tube furnace with the following schedule: a 15 min heating to 940 C - 945 C to melt most of the mixture, cooling at a rate 0.2 C/min to 900 C where crystals formed, cooling at 1 C/min to 700 C, 2 C/min to 400 C, and five more hours of furnace cooling to room temperature. This procedure relieved some of the inner stress and optimized the oxygen distribution and crystal structure. The x-ray dot maps and XPS show the crystals were chemically uniform with stoichiometries of (2212) and (2223) phase crystals. X-ray data recorded on a four circle diffractometer verified the (2212) single crystal was of high quality and no minor misoriented phase could be found.

In the (2223) phase crystals grown there are sometimes two or three subgrains with a few degrees of misorientation.

Pressure was generated in a diamond anvil cell<sup>14</sup> employing both hardened Be-Cu 25 alloy and Inconel gaskets. Samples were small, laminar single crystals whose sizes varied, but were less than 350  $\mu\text{m}$  on edge. Two different pressure transmitting fluids were used: light silicone diffusion pump oil for one sample and 4:1 methanol/ethanol for all the others studied. Pressure was measured using the ruby fluorescence technique<sup>15,16,17</sup> *in situ* at about 100 K and temperatures were maintained with a helium transfer refrigerator modified for optical measurements. At pressures above 0.1 GPa, there was a significant increase in sample pressure upon cooling, clearly demonstrating the importance of the *in situ* pressure measurement. Temperatures were measured with a calibrated silicon diode mounted on the cell close to the sample.

Superconducting transitions were detected by AC susceptibility techniques. A pair of coils, with 50 turns on the primary and 250 turns on the secondary and each wound to a shape conforming to that of the diamonds, was mounted around the diamond attached to the fixed end of the cell. These were connected to a Hartshorn AC susceptibility bridge.<sup>18</sup> Sinusoidal fields of approximately 0.2 Gauss rms were generated by a signal generator at about 2 KHz. Temperature sweeps were generally performed by warming from low temperatures at a rate of  $1.0 \pm 0.2$  K/min. Controlled cooling sweeps demonstrated no hysteresis within the temperature resolution of the experiment. Both real and imaginary components of the susceptibility were detected with a lock-in amplifier. Figure 1 shows several transitions observed in the real susceptibility component for sample 1 at various pressures. A transition width of approximately 2 K is found between the 90 and 10

percent temperatures. And there is essentially no change in this width to the highest pressure.

The results of experiments conducted on four samples are shown in Figure 2. Sample 1 was a single crystal in a BeCu gasket with silicone oil for a pressure transmitting medium and had an ambient pressure onset temperature of 112 K. A large initial positive slope of about 4 K/GPa is indicated. At higher pressures, the slope decreased and at the highest pressure dropped from 122.7 K at 3.7 GPa, to 121.3 at 4.8 GPa. It was thought that this might arise from some effect of the non-hydrostaticity of the fluid, but examination of the ruby fluorescence spectra showed no observable broadening within the precision of the spectrometer. Samples 2, 3 and 4 were studied using inconel gaskets and 4:1 methanol/ethanol fluid. They had ambient pressure onset temperatures of  $106.7 \pm 0.4$  K (extrapolated from a quadratic fit to high P data),  $114.0 \pm 0.2$  K, and  $107.2 \pm 0.2$  K, respectively. Each of these possesses a positive initial  $dT_c/dP$ . Values of 1.6 K/GPa, 2.0 K/GPa and 2.4 K/GPa were recorded for samples 2, 3 and 4 respectively and are consistent with previously reported values.<sup>9,10,11</sup> At higher pressures these samples clearly demonstrate a downward curvature over the pressure range attainable with this system, although the maximum pressure was not high enough to observe any decrease. A similar effect has been observed recently by Mori et al.<sup>12</sup> and Allgeier et al.<sup>13</sup> each using polycrystalline samples. Mori, et al. generated pressures with a cubic anvil device and with room temperature measurements of pressure based on bismuth fixed points. Allgeier et al. pressed the polycrystalline sample into a metal gasketed anvil cell but details of their pressure measurement were not given.



This remarkable pressure dependence can be explained in direct analogy with the dependence of  $T_c$  on the carrier concentration that is characteristic of many of the cuprate superconductors<sup>19</sup> and particularly in the work of Martin et al.<sup>8</sup> on the series of Tl cuprate superconductors with one, two and three Cu-O layers.

Recently Kresin and Moravitz<sup>20</sup> have explained the carrier dependence of the transition temperature in the cuprates, especially in the LaSrCuO "214" compound, by utilizing both the strong coupling BCS theory and the highly anisotropic quasi-2D Fermiology that exists because of the layered structure of the Cu-O planes. Using the strong-coupling Eliashberg form of the BCS theory, they find that  $T_c$  is a non-monotonic and very sensitive function of the Fermi wavevector  $k_F$ . This is due to the electron-phonon coupling parameter  $\lambda$  being proportional to  $k_F^2$  when  $k_F$  is smaller than a limiting value of the phonon momentum,  $q_c$ , for the most important phonon mode, and proportional to  $(k_F)^{-1}$  when  $k_F \gg q_c$ . Thus, as  $k_F$  crosses through  $q_c$ , the transition temperature is maximum and decreases on either side of this optimum condition. In a quasi 2D layered superconductor it has been shown that

$$(k_F)^2 = [2 \pi n c]$$

where  $n$  is the carrier concentration and  $c$  is the distance between conducting 2D subsystems.<sup>21</sup> Thus, not only is the transition temperature strongly affected by the carrier concentration,  $n$ , it is clearly just as strong a function of the interlayer spacing  $c$ . Therefore there should be a direct analogy between the dependence of  $T_c$  on  $n$  and on  $c$ .

The dependence on carrier concentration for the Tl "2212" compound has been measured by Martin et al.<sup>8</sup> and Shimakawa et al.<sup>7</sup> They clearly show that,

as made, this compound is "overdoped" as far as  $T_c$  is concerned. By a low temperature reducing anneal that removes oxygen and hence decreases  $n$ , Martin et al. found a transition temperature that rises very rapidly from about 96 K to a maximum of about 118 K and then starts to fall more slowly as the carriers are further removed. Thus  $k_F$  is larger than  $q_c$  to begin with and is reduced so that it crosses through  $q_c$  at some concentration giving rise to the non-monotonic dependence of  $T_c$  with carrier concentration. Similarly an increase of pressure reduces  $c$  and therefore  $k_F$ . The dependence of  $T_c$  on pressure should therefore mimic the dependence of  $T_c$  on  $n$ . The data in Fig. 2 are strikingly similar to the data in Table I in the Martin work. Of course for a quantitative comparison the Martin data would have to be plotted versus carrier concentration rather than the reducing time and the data presented here would have to be plotted versus  $c$  not pressure.<sup>22</sup> It is also possible that pressure may indirectly affect carrier concentration in addition to its very direct affect on  $c$ . Therefore it may be very difficult to get quantitative agreement with the theory unless the carrier concentration is directly measured as a function of pressure as well as oxygen reduction.

An interesting test of the theory would be to perform first an oxygen reduction and then a determination of the pressure dependence of  $T_c$ . If  $k_F$  is reduced to a value less than  $q_c$  by reduction, further decreases in  $k_F$  resulting from decreases in  $c$  should result in a monotonically decreasing critical temperature and a negative value of  $dT_c/dP$ .

This work was supported in part by the Office of Naval Research, DARPA, and SDIO. One of us (NEM) acknowledges support from an Office of Naval Technology Post Doctoral award.

## Figure Captions:

Fig. 1: Offset voltage vs. sample temperature for  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_x$  single crystal for 5 pressures to 48 kbar.

Fig. 2: Increase in  $T_c$  with pressure for 4 different single crystal samples of  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_x$

---

<sup>1</sup>C. Murayama, N. Mori, S. Yomo, H. Takagi, S. Uchida and Y. Tokura, *Nature* 339, 293 (1989).

<sup>2</sup>R. Griessen, *Phys. Rev. B* 36, 5284 (1987)

<sup>3</sup>E. N. Van Eenige, R. Griessen, R. J. Wijngaarden, J. Karpinski, E. Kaldis, S. Rusiecki and E. Jilek, *Physica C* 168, 482 (1990).

<sup>4</sup>E. Kaldis, P. Fisher, A. W. Hewat, E. A. Hewat, J. Karpinski and S. Rusiecki, *Physica C* 159, 668 (1989).

<sup>5</sup>Y. Yamada, T. Matsumoto, Y.. Kaieda and N. Mori, *Japan. J. Appl. Phys.* 29, L250 (1990).

<sup>6</sup>K. Murata, Y. Honda, H. Oysnsgi, Y. Nishihara, H. Ihara, N. Terada, R. Sugise, M. Hirabayashi, M. Tokumoto and Y. Kimura, *Bull. Electrotech. Lab.* 53, 37 (1989).

<sup>7</sup>Y. Shimakawa, Y. Kubo, T. Manako and H. Igarashi, *Phys. Rev. B* 40, 11400 (1989).

<sup>8</sup>C. Martin, A. Maignan, J. Provost, C. Michel, M. Hervieu, R. Tournier and B. Raveau, *Physica C* 168, 8 (1990).

<sup>9</sup>J. E. Schirber, B. Morosin and D. S. Ginley, *Physica C* 157, 237 (1989).

<sup>10</sup>J. Stankowski, B. Czyzak, M. Krupski, J. Baszynski, T. Datta, C. Almasan, Z. Z. Sheng and A. M. Hermann, *Physica C* 160, 170 (1989).

- 
- <sup>11</sup>J. L. Zhang, C. G. Cui, S. L. Li, Y. L. Zhang, X. R. Chang and Q. S. Yang, *Mod. Phys. Lett. B* 2, 879 (1988).
- <sup>12</sup>N. Mori, H. Takahashi, Y. Shimakawa, T. Manako and Y. Kubo, *J. Phys. Soc. Japan* 59, 3839 (1990).
- <sup>13</sup>C. Allgeier, R. Sieburger, H. Gossner, J. Diedrichs, H. Neumaier, W. Reith, P. Muller and J. S. Schilling, *Physica C* 162-164, 741 (1989)
- <sup>14</sup>E. F. Skelton, I. L. Spain and F. J. Rachford, in C. W. Chu and J. A. Woollam editors, *High Pressure and Low Temperature Physics*, 337, Plenum Publishing Company, New York (1978).
- <sup>15</sup>P. M. Bell and H. K. Mao, *Carnegie Inst. of Washington Yearbook*, 399 (1974).
- <sup>16</sup>R. A. Noack and W. B. Holzapfel in *High Pressure Science and Technology*, edited by K. D. Timmerhaus and M. S. Barber (Plenum Press, New York, 1979) Vol. 1, p.748.
- <sup>17</sup>I. F. Silvera and R. J. Wijngaarden, *Rev. Sci. Instr.* 56, 121 (1985).
- <sup>18</sup>E. Maxwell, *Rev. Sci. Instr.* 36, 553 (1965).
- <sup>19</sup>J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezing, T. C. Huang and S. S. P. Parkin, *Phys. Rev. Lett.* 61, 1127 (1988)
- <sup>20</sup>V. Kresin and H. Morawitz, *Solid State Commun.* 74, 1203 (1990)
- <sup>21</sup>V. Z. Kresin and S. A. Wolf, *J. Superconductivity* 1, 143 (1988).
- <sup>22</sup>Compressibility data have been collected recently from the same batch of samples used here at pressures to 50 GPa; these data are presently being analyzed in terms of the linear compressibilities and associated bulk moduli.



